INFLUENCE OF DIFFUSION ON THE ENERGY MIGRATION IN MIXED SOLUTIONS

By Z. VÁRKONYI

Institute of Experimental Physics, Attila József University, Szeged

(Received, November 25, 1968)

The quenching of luminescence of trypaflavine by rhodamine B in aqueous solutions was studied with quencher concentrations from 6×10^{-5} to 2×10^{-3} mole/litre in the viscosity interval 0,01—20 poise and at temperatures between 0 °C and 50 °C. The experimental results are discussed in terms of Förster's and Jabłoński's model. It has been found that the diffusion is not to be neglected in the region of lower viscosities and a quantitative relation taking the diffusion into account is given. The energy transfer proved to be greater even with respect to the diffusion than predicted by the theories of Förster and Jabłoński.

Introduction

According to FÖRSTER's theory of energy migration [1], [2] the probability of energy migration (if the mutual position of excited and quenching molecules is not altered in the excited state) can be expressed as follows:

$$n_{AL} = \frac{1}{\tau_{0A}} \left(\frac{R_0}{R}\right)^6 \tag{1}$$

where τ_{0A}, R and R_0 denote the mean life-time of the excited state of the molecule A in absence of the quenching molecule L, the mean distance between the excited molecule A^* and the quenching molecule L, and the critical distance, respectively.

$$R_0 = \sqrt[6]{\frac{9\overline{\varkappa^2}(\ln 10)^2 c^2 \tau_{0A} I_{\bar{\nu}}}{16\pi^4 n^4 (N')^2 \bar{\nu}_0^2}}\,. \tag{2}$$

Here c is the velocity of light in vacuum, n is the refractive index of solution, $N' = 6.02\times10^{20}$, $\varkappa$ is a constant depending on the mutual orientation of the interacting molecules (in solutions, supposing total randomness, $\overline{\varkappa^2} = 2/3$), $\bar{\nu}_0$ denotes the wave-number of pure electron transition and $I_{\bar{\nu}}$ is the so-called overlap-integral. According to FÖRSTER [3] the following relation exists between the relative yield η/η_0 of the mixed solution and the concentration c of the equimolar solution:

$$\frac{\eta}{\eta_0} = 1 - \sqrt{\pi}\,\frac{c}{c_0}\cdot e^{\left(\frac{c}{c_0}\right)^2}\left[1 - \Phi\left(\frac{c}{c_0}\right)\right] \tag{3}$$

where the constant c_0 is the so-called critical concentration, $\Phi(c/c_0)$ the error-function;

supposing a random distribution of the molecules, c_0 and R_0 are connected by the following relation

$$R_0^3 = \frac{3}{2\sqrt{\pi^3}} \frac{1}{c_0}. \tag{4}$$

Using Eq. (3) and the experimental values of η/η_0, c_0 can be empirically obtained and then R_0 can be calculated with Eq. (4) The comparison of the R_0 values obtained from Eq. (2) and (4) is very useful in examining the validity of Försters's theory. For non-equimolar solutions using FÖRSTER's [3] and KETSKEMÉTY's [4] considerations, R_0 can be calculated with the following relation:

$$R_0^6 = \frac{9\varkappa^2 c^4}{128\pi^4 n^2 N' \tau} \int_0^\infty f_{qA}(\nu) \varepsilon_L(\nu) \frac{d\nu}{\nu^4}. \tag{5}$$

Here $f_{qA}(\nu)$ is the emission quantum spectrum of the donor molecule, and $\varepsilon_L(\nu)$ denotes the decadic molar extinction coefficient of the acceptor molecule. In the systems studied the additivity relation between the spectra of mixed solutions is fulfilled ([5], [6]), the donor does not practically absorb in the overlap region and Beer—Lambert's law is valid. The validity of the restrictions made in Förster's theory has been proved by GALANIN [7], LATT [8], DREXHAGE [9] BOWEN and LIVINGSTONE [10]. They found a good agreement between the values of R_0 determined from the quenching curves and those calculated with Eq. (2) and came to the conclusion that the yield of migration of the excitation energy does not depend substantially on the viscosity of the solvent.

On the other hand, some authors *e.g.* WEINREB [11] and MELHUISH [12] found that the energy transfer is enhanced by an increasing rate of diffusion. Recently several papers [13], [14], [15] point to the fact that the diffusive displacement of the molecules during the life-time of the excited state cannot be neglected. In the modification of Förster's quenching theory by BAGDASARYAN and MULER [13] also the influence of diffusion is taken into consideration. They found that the energy transfer is more effective than it is expected from Förster's theory. FEITELSON [14] obtained similar results for a p-terphenyl-9-methylanthracene system. The quenching process was treated by JABŁOŃSKI [15] on the base of a simplified model of the luminescent centers, which consists of the excited luminescent molecule and the surrounding „active sphere" and may also contain a quenching molecule. Jabłoński came to the following relation:

$$\frac{\eta}{\eta_0} = \frac{1 - e^{-v}}{v}, \tag{6}$$

where $v = nv$, n is the concentration of the quencher and v denotes the volume of the active sphere, which can be determined empirically. Jabłoński's theory [15], [16] has been further developed by HEVESI [17], [18] and BOJARSKI [19], [21]. Taking into consideration the influence of diffusion, Hevesi rewrote Eq. (6) in the following form:

$$\frac{\eta}{\eta_0} = \frac{1 - e^{-ac}}{ac}, \tag{7}$$

where c is the molar concentration of the quencher and $a = N \cdot v$. The volume of the active sphere v is a given function of η_v and of τ. BOJARSKI [19]—[21] completed Jabłoński's theory considering a multilayer luminescent centrum as model and taking into consideration the oscillation in the concentration of quenchers beyond the active sphere.

Composition of the systems and experimental methods

Two dyes (trypaflavine and rhodamine B) were chosen as donor and acceptor, for which the luminescence spectrum of the donor and the absorption spectrum of the acceptor showed a considerable overlap. The viscosity of the solutions was varied in a mixture of glycerol and water by changing the glycerol concentration (0, 60 and 90%) and the temperature (273, 298 and 323 °K). Measurements were made in the viscosity interval from 0.01 to 20 P. The trypaflavine concentration was kept constant (1.25×10^{-4} mole/litre), the concentrations of rodamine B were 6.25×10^{-5}, $1{,}25 \times 10^{-4}$, 2.5×10^{-4}, 5×10^{-4}, 1×10^{-3} and 2×10^{-3} mole/litre, respectively. In order to obtain better solubility of dyes and stabilization of solutions 1×10^{-3} mole/litre HCl was added.

The dyes were purified by recrystallization until constancy of spectra; the glycerol was purified with vacuum distillation.

The spectra and the relative yields were measured using a plane-grating single-beam autocollimating spectrophotometer Optica Milano Type CF 4., with adequate attachments [22]. The temperature was kept constant by a Höppler-type ultrathermostat. The methods described in [23], [6] were used to evaluate the experimental results. Fluorescence spectra were corrected for reabsorption; correction for secondary luminescence could be neglected due to the experimental conditions [24].

Experimental results and discussion

The results are shown in Figs. 1—3. The measured relative yields are plotted as a function of $\log \gamma$, $\left(\gamma = \frac{c}{c_0}\right)$. The quenching curves calculated by using Eq. (3) are drawn with a solid line. It can be seen from the figures that at 273 °K the agreement between the measured and the calculated values is very good; it is less satisfactory at 298 °K, whereas at 323 °K considerable deviations are to be found.

The agreement between calculated and measured data at 273 °K was very good in all sets of solutions at every value of viscosity. This does not mean, however, that the quenching at this temperature does not depend on viscosity. Namely, a comparison of the values of R_F obtained from Eq. (4) using the empirical values of c_0 with the R_0 obtained from the spectra shows that the values of R_0 are much less than those of R_F[1]. Thus it can be only concluded from the figures that Förster's

[1] In the following the critical distances obtained with different methods are marked by different subscripts. R_0 means the critical distance calculated with Eq. (5), R_F that calculated with Eq. (4), R_{BM} the value calculated with Eq. (8) in [13], R_J with Eq. (5) in [16], R_B with Eq. (22) in [20] and R_V calculated with Eq. (9).

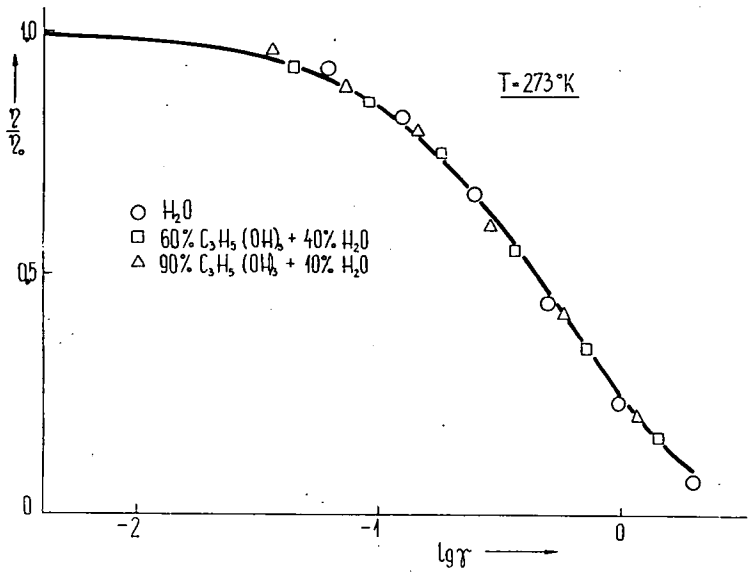

Fig. 1

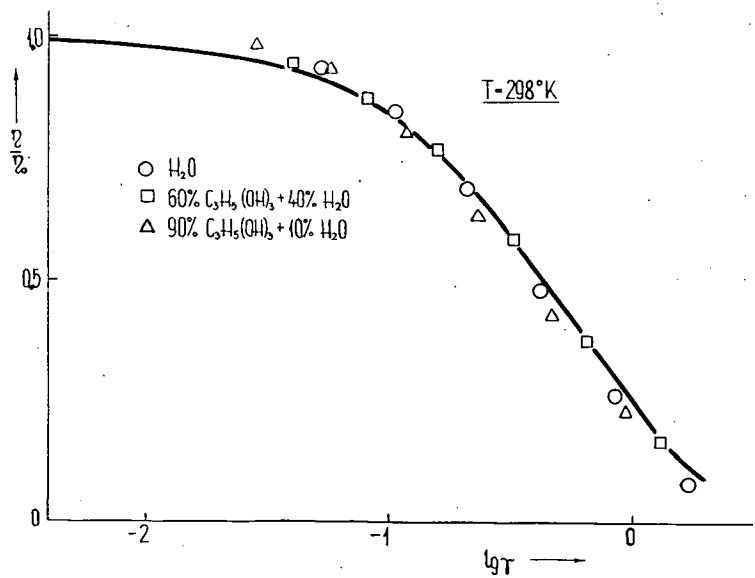

Fig. 2

theory gives a good description of the slope of the quenching curves for the temperature 273 °K.

According to the data of Table I the energy migration is more effective in

Table I

Solution	O_K^T	R_0	R_F	R_{BM}	R_J	R_B	R_V
		Å					
H_2O	273	59.0	75.8	73.4	115.5	75.7	58.4
	298	60.0	72.4	71.0	108.6	72.4	56.6
	323	58.2	61.2	62.5	90.9	63.4	54.9
60% glycerol	273	57.3	68.1	65.3	99.2	69.2	65.3
	298	58.2	66.2	63.4	94.3	66.2	59.3
	323	55.9	59.0	58.7	89.3	61.2	55.2
90% glycerol	273	56.8	63.4	61.4	92.5	64.3	62.5
	298	56.2	59.1	60.0	88.5	63.5	61.1
	323	56.6	57.9	55.5	82.2	60.0	59.9

solutions of lower than in those of higher viscosity. For 323 °K (Fig. 3), Eq. (3) does not give an adequate description of the real shape of the quenching curve (marked by the experimental points in the figure). At low quencher concentrations the experimental points lie systematically above the theoretical curve, at high concentrations below. The data of Table I show a decrease of R_F with viscosity also at this temperature, but the dependence on viscosity is less pronounced here than at 273 °K. Essentially the same was observed for the temperature 298 °K (Fig. 2).

It can also be seen from Table I, that the values of R_0 decrease with increasing

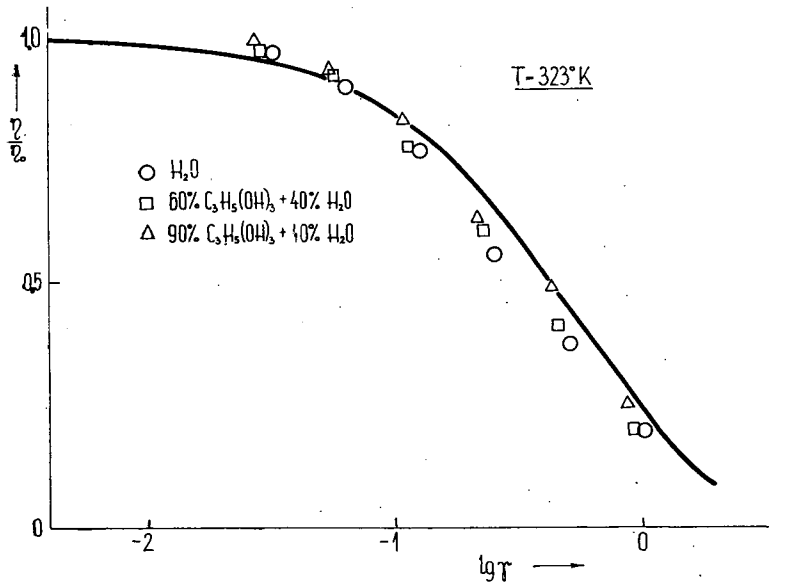

Fig. 3

temperature for the same set of observed solutions. According to the results of SZALAY and KOZMA [25] with glycerol solutions of fluorescein, rhoduline orange and rhodamine B, R_0 is practically the same, whether the energy transfer occurs before or after reaching the vibrational equilibrium. The finding that the R_0 calculated from Eq. (5) and the R_F obtained from Eq. (4) are different (namely $R_0 < R_F$, *i.e.* the energy transfer is more effective than expected from Förster's theory) has been described also is the case of other systems [1], [26], [27].

A better agreement can be obtained if the critical distance is determined with the relations obtained by using the modifications of Förster's theory [13], [15], [16], [17], [20]. These values are also given in Table I. The values R_{BM}, R_J, R_B obtained from the quenching curves were greater for all solutions than those calculated with Eq. (5), despite the refinement of the quenching theories.

In order to ascertain whether the higher rate of energy transfer *i.e.* the difference between R_0 and the experimental R_B is caused by the increase in the duffusion rate, the volume

$$V^* = \frac{4}{3}\pi R_V^{*3} \tag{8}$$

has been substituted instead of the quenching volume V. R_V^* is composed of the radius R_B of the active sphere and of the diffusive displacement determined with the formula $r \equiv (\overline{r_D^2})^{\frac{1}{2}} = \frac{kT\tau}{\pi\eta_v\sigma}$ [21]: $R_V^* = R_B + r$. Here σ is the radius of the excited molecule considered to be spherical. Thus the critical distance is:

$$R_V = \left(\frac{3v}{4\pi N' c_L}\right)^{\frac{1}{3}} - \left(\frac{k}{\pi\sigma}\frac{T}{\eta_V}\right)^{\frac{1}{2}}, \tag{9}$$

where c_L is the concentration of the quencher. According to [20] $R_V = 1.204 R_F$. As it was to be expected, the deviations of R_V from R_B are greater in aqueous solutions at lower viscosities. These deviations are primarily due to the fact that the mean displacements of the molecules in aequous solutions (15.6 Å, 23.1 Å and 27.1 Å) are comparable with the critical distance. The decrease of the distances R_F compared with R_B is so considerable that the values obtained are less then the R_0 calculated with Eq. (4). On the other hand, a good agreement between R_0 and r_V can be obtained, if the latter is calculated with $\sigma = 6$—7 Å, which also seems to be acceptable from a physical point of view, instead of the value $\sigma = 5$ Å used in [28]. In the case of solutions of higher viscosity the values of R_V are not remarkable changed by calculating with Eq. (9), but the inequality $R_0 < R_V$ exists.

It can be inferred from our results that though the diffusion plays a role in energy migration, especially in solutions of low viscosity, the deviation between the critical distances calculated with both methods, *i.e.* with Eq. (5) and from the quenching curves, cannot be explained merely by the neglection of diffusion. Further investigations to clear up the cause of these deviations are in progress.

Appendix

In the following we give some of the relations between the different critical distances characteristic for energy migrations, as well as those obtained in the present paper. BOJARSKI's [31] experimental results based on the shell model $R_J = 1.326R_F$; BOJARSKI's [32] calculations with a refined shell model $R_J = 1.466R_F$; according to BOJARSKI [20] $R_B = 1.204R_F$; SZALAY and SÁRKÁNY [29] calculated $R_J = 1.367R_F$; according to ERIKSEN [30] $R_J = 1.49R_F$ for low concentrations and $R_J = 1.41R_F$ for high concentrations. As a result of our own calculations $R_{BM} = 0.98R_F$, $R_J = 1.474R_F$, $R_B = 1.232R_F$, $R_V = 0.820R_F$ for low viscosities, and $R_V = 0.967R_F$ for high viscosities.

* * *

The author is indebted to thanks to Professor Dr. A. BUDÓ, Director of the Institute, for his interest in this work. Thanks are due to Professor L. SZALAY for his continued help in the course of experiments and to Professor I. KETSKEMÉTHY for his valuable advices.

References

[1] *Förster, Th.:* Z. Naturforsch. **4a**, 321 (1949).
[2] *Förster, Th.:* Z. Elektrochem. **53**, 93 (1949).
[3] *Förster, Th.:* Floureszenz Organischer Verbindungen (Vandenhoeck und Ruprecht, Göttingen, 1951).
[4] *Ketskeméty, I.:* Z. Naturforsch. **17a**, 666 (1962).
[5] *Ketskeméty, I.:* Acta Phys. Hung. **10**, 429 (1959).
[6] *Dombi J.:* Energy transfer processes in luminescent mixed solutions. Thesis for the degree of candidate of physical sciences, Szeged (1967).
[7] *Galanyin, M. D.:* Zs. Exp. Teor. Fiz. 28, 485 (1955).
[8] *Latt, S. A., H. T. Cheung, and E. R. Blant:* J. Ann. Chem. Soc. **87**, 995 (1965).
[9] *Drexhage, K. H., M. M. Zwick and H. Kuhn:* Ber. Bunsenges. f. Phys. Chem. **67**, 62 (1963).
[10] *Bowen, E. J. and R. Livingston:* J. Am. Chem. Soc. **76**, 6300 (1954).
[11] *Weinreb, A.:* J. Chem. Phys. **35**, 91 (1961).
[12] *Melhuish, W. H.:* J. Phys. Chem. **67**, 1681 (1963).
[13] *Bagdasaryan, H. C., A. L. Muler:* Opt. i Spektr. **18**, 990 (1965).
[14] *Feitelson, J.:* J. Chem. Phys. **44**, 1497 (1966).
[15] *Jabłoński, A.:* Acta Phys. Polon. **13**, 175 (1954).
[16] *Jabłoński, A.:* Bull. Acad. Polon. Sci. Ser. Sci. Math. Phys. Astron. **6**, 663 (1958).
[17] *Hevesi, J.:* Quenching of the photoluminescence of viscous dye-stuff solutions by foreign substances. Thesis for the degree of candidate of physical sciences, Szeged (1965).
[18] *Hevesi, J.:* Acta Phys. et Chem. Szeged **8**, 15 (1962).
[19] *Bojarski, C.:* Acta Phys. Polon. **19**, 631 (1960).
[20] *Bojarski, C.:* Acta Phys. Polon. **30**, 169 (1966).
[21] *Bojarski, C.:* Proceedings of the International Conference on Luminescence, 1966. (Akadémiai Kiadó, Budapest, 1968) Vol. 1. p. 446.
[22] *Ketskeméty, I., J. Dombi, J. Hevesi, R. Horvai und L. Kozma:* Acta Phys. et Chem. Szeged, **7**, 88 (1961).
[23] *Ketskeméty, I.:* Physical basis of the luminescence of solutions. Thesis for the degree of doctor of physical sciences, Szeged (1964).
[24] *Budó, A.:* Magyar Fizikai Folyóirat **9**, 269 (1961).
[25] *Szalay, L., L. Kozma:* Acta Phys. Hung. **20**, 389 (1966).
[26] *Szvesnyikov, B. Ja., P. I. Kudrjasov, L. A. Lumerova:* Opt. i Szpektr. **9**, 203 (1960).
[27] *Weinreb, A.:* J. Chem. Phys. **35**, 91 (1961).

[28] *Szalay, L.:* Investigations on fluorescence polarization of solutions. Thesis for the degree of doctor of physical sciences, Szeged (1964).
[29] *Szalay, L., B. Sárkány:* Acta Phys. et Chem. Szeged **8**, 23 (1962).
[30] *Eriksen, E. L.:* Phys. Norvegica **2**, 189 (1967).
[31] *Bojarski, C.:* Ann. Phys. **12**, 253 (1963).
[32] *Bojarski, C.* · Acta Phys. Polon. **25**, 179 (1964).

ВЛИЯНИЕ ДИФФУЗИИ НА ПЕРЕДАЧУ ЭНЕРГИИ В СМЕШАННЫХ ЛЮМИНЕСЦИРУЮЩИХ РАСТВОРАХ

З. Варкони

Исследовалось тушение флуоресценции трипофлавина родамином в глицеринно-водном растворе, при концентрации $6 \cdot 10^{-5}$—$2 \cdot 10^{-3}$ м/л тушителя, в области вязкости раствора 0.01—20 пз. и в интервале температуры 0—50 °С. Полученные экспериментальные данные интерпретируют по модели Ферстера и Яблонского.

Установили, что при низких значениях вязкости следует учитывать влияние диффузии, дали количественное соотношение этого явления. Степень передачи энергии с учетом диффузии больше, чем можно было бы ожидать на основе теории Ферстера и Яблонского.